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## A THERMAL STUDY OF POLYMINERAL CLAYS OF THE GZHEL' DEPOSIT

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A thermal analysis of clays of the Gzhel' deposit is performed and their mineral composition is established. The effect of various admixtures and minerals and the dispersity on the behavior of the clays during heating is described.

The heating behavior of kaolins and refractory clays has been studied in many works.

As a rule, clays are represented by polymineral formations. The effects of the blend components and the admixtures can be manifested in different ways. Upon heating they can react with the clay mineral, can be thermally independent, or can catalyze the processes that occur in the clay mineral. A considerable difference in the behavior of low-melting clays in heating as a function of the mineral composition has been observed in [1]. For example, in montmorillonite clay (from the Spass-Kamenskoe deposit) dehydration starts at 220°C, whereas in hydromica clay (from the Bun'kovskoe deposit) it starts at about 420°C.

Taking into account the wide palette of Gzhel' montmorillonite clays and the influence of hematite on the color characteristics [2] we chose three groups of clay, hematite, and goethite for a thermal study. The group of light clays included gray, green, and gray-green varieties, the group of red clays included varieties colored from light-red to brown, and the group of particolored clays included pink, lilac, and black-gray-pink varieties.

The thermal study was performed with the help of a "Bahr" device. Specimens 50–60 mg in mass with particles milled to a size of 0.2 mm were heated at a temperature ranging from room to 1200°C at a rate of 10 K/min. The tested specimen had the shape of the alumina crucible, namely, a cylinder. The error of measurement was 0.5°C. The standard for the DTA curve was calcined aluminum oxide; in the determination of iron compounds in the clay we used thermograms of hematite and goethite.

The thermal analysis of hematite (Fig. 1) showed the presence of smeared peaks at 292 and 340°C, which correspond to a weak exothermic effect (oxidation of wustite at

292°C) and an endothermic effect (transformation of  $\gamma\text{-Fe}_2\text{O}_3$  into  $\alpha\text{-Fe}_2\text{O}_3$  at 340°C). The second well-manifested endothermic effect at 597°C is connected with the transformation of  $\alpha\text{-Fe}_2\text{O}_3$  into  $\gamma\text{-Fe}_2\text{O}_3$  [3].

It is known that the presence of  $\text{Fe}^{2+}$  ions in the clay promotes the appearance of new phases. It should be noted that the formation of wustite from hematite is accompanied by the emission of gas [4].

The first endothermic effect in the thermogram of goethite was determined at a temperature of 100°C and corresponded to the removal of free water, and the second powerful endothermic effect at 365°C corresponded to the dehydration of goethite and the formation of  $\alpha\text{-Fe}_2\text{O}_3$ . At 605°C we observed a poorly manifested peak corresponding to the endothermic effect of the transformation of  $\alpha\text{-Fe}_2\text{O}_3$  into  $\gamma\text{-Fe}_2\text{O}_3$ .

The thermal study of the light clays (gray, green, and gray-green) showed that their heating behavior differed to a certain degree.

It is known that dehydration of clay minerals is accompanied by an endothermic effect observed in a wide temperature range (450–700°C) and in some cases even at up to

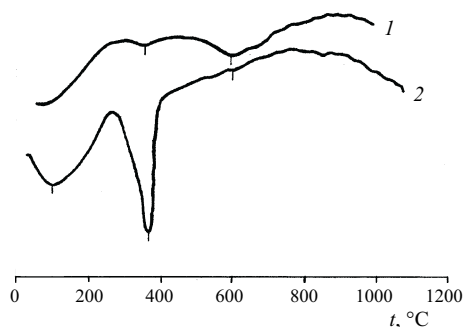


Fig. 1. Thermograms of hematite (1) and goethite (2).

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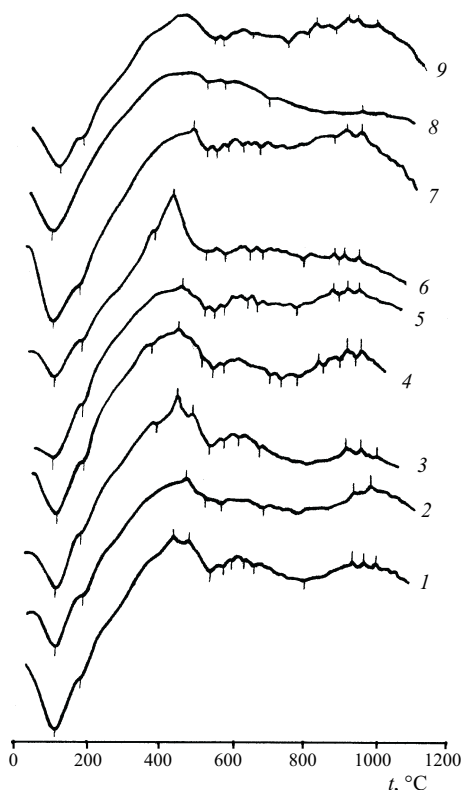
900°C. The dehydration of the clay depends on the kind of clay minerals in the composition of the clay. Characteristic temperatures of dehydration of clay minerals are up to 300°C for montmorillonite and illite-like hydromicas (the water is predominantly removed at up to 120°C), 400–700°C for kaolinized hydromicas, and 470–550°C for kaolinite [5].

Free water was removed from the gray-green clay (Fig. 2) at 107°C; the weak endothermic effect at 187°C corresponded to further removal of water (contained between the layers). The quite smeared endothermic affect at 350°C indicated the presence of iron oxides in the gray-green clay in the form of admixtures but in an inconsiderable amount. In addition, the thermogram of this clay had a well manifested exogenic effect at a temperature of 453°C and a binary endogenic effect in the range of 528–540°C, which corresponded to oxidation of the organic admixtures and removal of the  $(\text{OH})^-$  group with disruption of the montmorillonite lattice. The binary endogenic effect was caused by the presence of kaolinite in the gray-green clay. The weak peak at 501°C corresponded to the exogenic effect of oxidation of pyrite to hematite. A polymorphic transformation of quartz was established at 580°C, removal of the  $(\text{OH})^-$  group from the hydromica occurred at 616°C, and transformation of the  $\alpha\text{-Fe}_2\text{O}_3$  of hematite and other iron compounds into  $\gamma\text{-Fe}_2\text{O}_3$  occurred at 670°C. The montmorillonite lattice broke up at 800°C, the amorphous products of the decomposition of montmorillonite crystallized at 920°C, and the structure of the hydromica broke up fully and the amorphous products of the break up recrystallized at about 945°C. The weak peak at 1000°C corresponded to recrystallization of the amorphous products of the decomposition of kaolinite and formation of mullite nuclei.

The thermogram of the green clay differs from that of the gray-green clay in two respects, namely, the absence of a well-manifested peak at 400–450°C (exothermic effect) and the presence of an endothermic affect at 540°C. This is explainable by the absence of organic admixtures in the green clay and the inconsiderable removal of  $(\text{OH})^-$  ions from the kaolinite. It is known that oxidation of organic admixtures is accompanied by an exothermic effect at 300–400°C. However, under rapid heating of the clay the organic admixtures burn off at a higher temperature. In other respects the thermogram of the green clay virtually repeats that of the gray-green clay.

The thermal study of the gray clay showed the presence of all the phenomena typical of the gray-green and green clays. For example, we determined a quite smeared exothermic effect at 430°C and a well-manifested endothermic effect at 543°C, characteristic of the green and gray-green clays.

Thus, we can speak of like behavior of the light clays (gray, green, and gray-green) in heating and, consequently, of the similarity of their mineral composition and admixtures, although in the green clay we established the absence of organic admixtures and kaolinite.

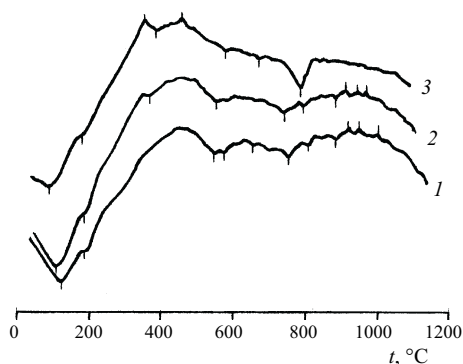


**Fig. 2.** Thermograms of clays of the Gzhel' deposit: 1) gray; 2) green; 3) gray-green; 4) pink; 5) lilac; 6) black-gray-pink; 7) brown; 8) treated with HCl; 9) red.

The thermal analysis of the red clay showed that water is removed from it at 120–187°C, the iron compounds oxidize at 330°C, the endothermic effect at 523°C corresponds to removal of  $(\text{OH})^-$  ions from montmorillonite, and kaolinite dehydrates at 546°C. A polymorphic transformation of  $\beta$ -quartz occurs at 571°C, removal of  $(\text{OH})^-$  from hydromica occurs at 603°C, and transformation of  $\alpha\text{-Fe}_2\text{O}_3$  of hematite and other iron compounds into  $\gamma\text{-Fe}_2\text{O}_3$  occurs at 650°C. The endothermic effects correspond to dissociation of calcite, removal of water from the talc-like layer, and break up of the montmorillonite lattice, whereas the exothermic effects at 823, 913, 940, and 1000°C correspond to disruption of the chlorite structure with formation of a mineral with an olivine structure, crystallization of the amorphous products of the decomposition of montmorillonite, recrystallization of the amorphous products of the decomposition of hydromica, and formation of mullite nuclei.

Thus, we can speak about the presence of carbonate admixtures in the red clay as well as montmorillonite, kaolinite, hydromica, chlorite, and hematite minerals.

The thermal study of the brown clay showed that it behaves like the red clay when heated but with a slight difference. This is indicated by the thermogram of the brown clay, which does not bear endothermic effects at 761 and 806°C, which confirms the absence of carbonate admixtures and



**Fig. 3.** Thermogram of red clay of the Gzhel' deposit: 1 and 2) before and after dressing; 3) remainder on screen No. 05.

chlorites in the clay, while the detected endothermic effect at 495°C indicates the presence of pyrite. This means that the brown clay differs from the red one by the presence of pyrite.

It should be noted that treatment of the red clay by a solution of HCl disrupts the montmorillonite, carbonates, chlorites, and hydromica. If we compare the thermograms of the red clay before and after the HCl treatment, we will see that the second endothermic effect, which corresponds to removal of the interlayer water from montmorillonite and hydromica, is absent on the curve of the red clay treated by HCl in the region of low temperatures and that the thermic effects present in the thermogram of the red clay before the HCl treatment are absent. In addition, we can see that the HCl-treated thermogram of the red clay bears endothermic effects (528, 576, and 683°C) connected with full break up of the montmorillonite lattice, polymorphic transformation of quartz, and transformation of  $\alpha\text{-Fe}_2\text{O}_3$  into  $\gamma\text{-Fe}_2\text{O}_3$ ; the preservation of the endothermic effect at 980°C reflects the crystallization of the amorphous products of the decomposition of kaolinite and the formation of mullite nuclei. It follows that the red clay treated with HCl preserves quartz, hematite, and, partially, montmorillonite and kaolinite.

The results of the thermal analysis of particolored clays (lilac, pink, black-gray-pink) were influenced by both the mineral composition and the admixtures. The thermograms of the pink and black-gray-pink clays were rather close and differed only in the absence of endothermic effects on the curve of the black-gray-pink clay that corresponded to dehydration of kaolinite and dissociation of calcite. We can thus state that the pink and black-gray-pink clays do not contain carbonates or kaolinite.

The lilac clay, in contrast to the other particolored clays, does not bear goethite or organic admixtures. The low intensity of the effect on the curve of the lilac clay corresponding to dehydration of chlorite and formation of a mineral with an olivine structure indicates a low chlorite content. It should be noted that the lilac clay contains pyrite, because we have discovered an exothermic effect at 463°C, which indicates oxidation of pyrite.

In all the particolored (black-gray-pink, pink, lilac) clays the adsorbed and interlayer water is removed at 107 – 192°C, dehydration of montmorillonite and kaolinite occurs at 524 – 550°C, a modification transformation of quartz occurs at 575 – 580°C, dehydration of hydromica occurs at 601 – 655°C, transformation of  $\alpha\text{-Fe}_2\text{O}_3$  into  $\gamma\text{-Fe}_2\text{O}_3$  occurs at 650 – 683°C, and disruption of the structure of montmorillonite and recrystallization occur at 895 – 900 and 910 – 918°C.

In order to study the behavior of clays of different dispersity under heat treatment we chose the red clay of the Gzhel' deposit, crushed it, and concentrated it with the help of screen No. 05. The remainder obtained on screen No. 05 and the clay before and after the concentration were subjected to a thermal analysis (Fig. 3).

It follows from the results of these studies that a considerable amount of admixtures (carbonates, organic inclusions, and gypsum) is removed from the clay due to its concentration, which is reflected by the endothermic effect at 780°C and the well-manifested peaks of exothermic effects in the region of 342 and 450°C in the thermogram of the remainder on the screen. In addition, the enrichment of the red clay is accompanied by removal of quartz and goethite together with the admixtures. For example, on curve 3 (see Fig. 3) we determined an endothermic effect that corresponded to hydration of goethite at 384°C and to a polymorphic transformation of quartz at 578°C.

Curve 2 (see Fig. 3) exhibits a temperature shift toward diminished dissociation of calcite and dehydration of chlorites. Removal of the adsorbed and interlayer water from the enriched clay occurs in the range of 107 – 185°C, dehydration of goethite occurs at 367°C, dehydration of montmorillonite occurs at 552°C, the weak endothermic effects at 740, 797, and 885°C correspond to dissociation of calcite, removal of water from the talc-like layer, and disruption of the montmorillonite lattice, and the exothermic effects at 910, 978, and 1000°C are connected with crystallization of the amorphous products of the decomposition of montmorillonite, hydromica, and kaolinite. Consequently, the enriched red clay retains an inconsiderable amount of carbonates and a lowered content of quartz; the gypsum admixtures are fully removed.

We established that the processes in the enriched red clay (the beginning of removal of adsorbed water, the dissociation of calcite, the break up of the structure of the chlorites) occur at lower temperatures than in the unenriched clay. This can be explained by the fact that the processes in the coarser fractions shift toward high temperatures. Moreover, this agrees with the fact that the interaction between the components of the mechanical mixture occurs at high temperatures or in colloidal-disperse formations. A thermodynamically permissible solid-phase interaction between the substances is determined by two factors, namely, the size of the surface of contact between the particles and the state of the crystal structure

TABLE 1

Reactions that occur in heated clays	Thermic* effects, °C, in clays										
	gray	green	gray-green	red	brown	black- gray-pink	lilac	pink	red before en- richment	red after enrichment on screen No. 05	remainder on screen No. 05
Removal of adsorbed water	110(–)	110(–)	107(–)	120(–)	107(–)	107(–)	107(–)	118(–)	120(–)	107(–)	82(–)
Removal of interlayer water	182(–)	192(–)	187(–)	187(–)	192(–)	187(–)	192(–)	184(–)	187(–)	185(–)	185(–)
Disruption of the gypsum structure	Not determined										342(+)
Dehydration of goethite	Not determined		390(–)	Not determined		387(–)	Not de- termined	370(–)	Not de- termined	367(–)	384(–)
Oxidation of organic admixtures	430(+)	Not de- termined	453(+)	The same		432(+)		The same		451(+)	Not determined
Oxidation of pyrite to hematite	Not de- termined		467(+)	501(+)	Not de- termined	495(+)	Not de- termined	463(+)	Not determined		
Dehydration of montmorillonite	528(–)	523(–)	528(–)	523 (–)	528(–)	528(–)	528(–)	524(–)	Low-in- tensity effect	520(–)	Not de- termined
Dehydration of kaolinite	543(–)	Not de- termined	540(–)	546(–)	550(–)	Not de- termined	550(–)	546(–)		546(–)	552(–)
Modification transformation of quartz	568(–)		570(–)	580(–)	571(–)		576(–)	580(–)	576(–)	575(–)	571(–)
Dehydration of hydromica	632(–)	628(–)	616(–)	603(–)	620(–)	655(–)	640(–)	601(–)	Not de- termined	610(–)	Not de- termined
Transformation of α-Fe <sub>2</sub> O <sub>3</sub> from hematite and other iron compounds into γ-Fe <sub>2</sub> O <sub>3</sub>	660(–)	680(–)	670(–)	650(–)	680(–)	683(–)	675(–)	650(–)		650(–)	
Dissociation of calcite	Not determined			761(–)	Not determined		780(–)	766(–)	761(–)	740(–)	Strong effect 780(+)
Removal of water from the talc-like layer	Low-intensity effect			806(–)	Low-in- tensity effect	800(–)	Low-in- tensity effect	781(–)	806(–)	797(–)	Not de- termined
Disruption of the structure of chlorites and formation of a mineral with an olivine structure	The same			823(+)		810(+)		836(+)	823(+)	813(+)	
Full disruption of the structure of montmorillonite	800(–)	780(–)	806(–)	883(–)	876(–)	895(–)	895(–)	900(–)	883(–)	885(–)	The same
Crystallization of amorphous products of the decomposi- tion of montmorillonite	930(+)	940(+)	920(+)	913(+)	920(+)	910(+)	916(+)	918(+)	913(+)	910(+)	"
Full disruption of the structure of hydromica	950(–)	954(–)	940(–)	930(–)	Low-intensity effect			945(–)	Low-intensity effect		"
Recrystallization of amorphous products of disruption of hydromica	966(+)	960(+)	945(+)	940(+)	958(+)	946(+)	946(+)	955(+)	940(+)	958(+)	"
Crystallization of amorphous products of decomposition of kaolinite and formation of mullite nuclei	996(+)	Weak effect 980(+)	1000(+)	1000(+)	Not determined				1000(+)	1000(+)	"

\* (+) is used for "exothermic effect" and (–) is used for "endothermic effect."

of the reacting substances. The more deformed the structure, the easier the interaction between the substances [6].

The results of the thermal study of polymineral clays of the Gzhel' deposit are presented in Table 1.

It can be seen that the processes that occur in heated clays unite some of their types, for example, removal of the adsorbed and interlayer water (82 – 192°C), dehydration of montmorillonite and hydromica (520 – 528°C and 610 – 655°C), the modification transformation of quartz (568 – 580°C), transformation of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> of hematite and other iron compounds into  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (660 – 700°C), recrystallization of the amorphous products of the disruption of the hydromicas (940 – 978°C), and full break up of the structure of montmorillonite and crystallization of the amorphous products of the decomposition of montmorillonite in a wide temperature range (800 – 900°C). This temperature shift by 100°C can be explained by the difference in the types of montmorillonite. The structure of the montmorillonite with Ca<sup>2+</sup> ions breaks up at a lower temperature (800 – 806°C) than that of the montmorillonite with Na<sup>+</sup> ions (876 – 900°C).

Thus, the results of the thermal analysis agree with the data of the x-ray study made in [2] and confirm the

polymineral nature of the Gzhel' clays and the presence of various admixtures in them.

The Gzhel' clays used for the production of bricks can be used for manufacturing floor tile, facing tile, roof tile, and majolica articles for household and decorative purposes. However, the special features of the Gzhel' clays should be taken into account.

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